MOLECULAR WEIGHT AND PARTICLE SIZE OF POLYELECTROLYTES BY LIGHT SCATTERING

BY

CHARLES LaVERNE PAINTER

A.B., Fort Hays Kansas State College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

Polyelectrolytes are polymers which are capable of ionizing to various extents in polar solvents such as water. Since they act simultaneously as high polymers and as electrolytes, they exhibit many interesting and unusual properties. Polyacrylic acid is a simple example of these polyelectrolytes. Its ionization, increased by dilution or addition of base, produces a change in particle size due to the electrostatic forces involved. If a divalent base is added there will be an opportunity for cross-linking to occur, which will result in high molecular weights and large particle sizes.

Light scattering methods have been developed and applied by Debye (1) (2) and others (3) (4) (5) (6) for determining the particle size and molecular weight of ordinary uncharged polymers. The experimental qualities which must be measured are the absolute ninety degree scattering as a function of concentration and wavelength and the refractive index difference of solution and solvent. This investigation concerns the application of light scattering methods in the study of particle size and molecular weight changes of polyacrylic acid and its salts.

Results

A light scattering instrument designed to measure only the conventional ninety degree scattering has been constructed and calibrated.

The molecular weight and particle size were measured for two polyacrylic acids in the pure state. The first was found to have a molecular weight of 12,500 and a particle size small compared to the wavelength of the incident light, i.e., less than about 400 Angstroms. The second had a molecular weight of 20,700 and the particle size at infinite dilution was 830 Ang-

stroms. The molecular weight was found to remain approximately constant over a low concentration range whereas the particle size decreased linearly. Comparison of the experimental data with theoretical considerations indicate that at infinite dilution the particles exist as rigid stick molecules. As the concentration is increased they tend to coil up.

The behavior of polyacrylic acid partially neutralized with barium hydroxide has been studied. It was found that intermolecular cross-linking occurs most favorably at low polyacrylic acid concentrations. Here the molecule is expanded and the distance between carboxyl groups on the molecule is increased. The barium ions which combine with the acid cannot undergo intramolecular cross-linking so easily, and consequently, more of them cross-link with other molecules. This results in a gradual increase in particle size and molecular weight until the point is approached at which the particles precipitate from the solution. At higher concentrations the opposite effect predominates and there is very little cross-linking until the precipitation point is nearly reached.

The particle size and molecular weight of polyacrylic acid was studied as a function of neutralization with sodium hydroxide. Particle sizes far too large (3600 Angstroms) to be explained by an uncoiling of the molecule were found. The observed molecular weights were correlated with the particle sizes to confirm the theory of Staudinger (7) that clusters are formed in these solutions. These clusters begin to break up when large amounts of sodium hydroxide are present.

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VITA

The author was born near Healy, Kansas on August 27, 1918. He attended the local primary and secondary schools. His high school education was completed at Hays, Kansas in 1936. That same year he enrolled in the Fort Hays Kansas State College. The degree of Bachelor of Arts was awarded him in February, 1941. He entered the United States Naval Reserves as an Ensign in 1943 and served for two and one-half years. His duties involved radar maintenance and operational instruction. Upon discharge in 1946 he entered the Graduate College of the University of Illinois. He has held a Research Assistantship in Chemistry on the U. S. Government Rubber Research Program since March, 1948. The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma.

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